Investigation of adsorbent for a measurement of snow specific surface area by the gas adsorption method

Akihiro Hachikubo [1,*], Satoru Yamaguchi [2], Hayato Arakawa [3], Tomonori Tanikawa [4], Masahiro Hori [4], Konosuke Sugiura [5], Masashi Niwano [6], Katsuyuki Kuchiki [6] and Teruo Aoki [6]
[1] Kitami Institute of Technology, Kitami, Japan
[2] National Research Institute for Earth Science and Disaster Prevention, Nagaoka, Japan
[3] Yagai-Kagaku Co., Ltd., Sapporo, Japan
[4] Japan Aerospace Exploration Agency, Tsukuba, Japan
[5] Japan Agency for Marine-Earth Science and Technology, Yokosuka, Japan
[6] Meteorological Research Institute, Tsukuba, Japan

ABSTRACT: The specific surface area (SSA) of snow has been of particular interest to researchers because SSA strongly relates with snow albedo and is a better indicator of the complexity of snow as compared to grain size. We adopted the Brunauer–Emmett–Teller (BET) method for gas adsorption analysis in order to measure the SSA of synthetic ice particles and natural snow. Methane is a suitable adsorption gas for a porous material with a relatively small SSA, and is hence primarily used in the experiments. The repeatability of the SSA measurement in our system using methane was approximately 3%. The SSA obtained by the BET method agreed fairly well with the SSA obtained from section planes and also showed good correlation with the grain size obtained from microphotographs. We also examined krypton and hexane as new adsorbents. Methane and krypton require liquid nitrogen as a cryogen for snow samples, which makes it difficult to perform gas adsorption analysis in fieldwork. Because the vapor pressure of hexane is 1,717 Pa at −21.3 °C, which is the eutectic point of a mixture of NaCl and H_2O, a mixture of salt and snow is sufficient as a cryogen. We obtained reasonable BET curves using hexane, although the effect of water-vapor pressure (92 Pa at −21.3 °C) should be taken into consideration.

KEYWORDS: SSA, BET, methane, krypton, hexane

1 INTRODUCTION

The specific surface area (SSA) of snow is defined as its surface area [cm^2] per unit mass [g]. The SSA of snow strongly relates to snow albedo and is a better indicator of the complexity of snow as compared to grain size. A procedure to measure the SSA of snow by the Brunauer–Emmett–Teller (BET) method (Brunauer et al., 1938) has been developed and applied in the work of forerunners (e.g., Chaix et al., 1996; Hanot and Dominé, 1999; Dominé et al., 2001; 2006; Legagneux et al., 2002).

Methane is an adsorption gas suitable for a porous material with a relatively small SSA. The above-mentioned French researchers first applied methane to measure the SSA of snow and obtained desirable results. Legagneux et al. (2002) showed SSA values of snow from 100 to 1,580 $cm^2\ g^{-1}$. The most important factor to measure the SSA of snow is a the choice of adsorbent, which should exhibit a vapor pressure around 1 kPa at the temperature of the cryogen (e.g., liquid nitrogen). The vapor pressure of methane is 1,294 Pa at −195.8 °C.

On the other hand, krypton is a well-known adsorbent and is suitable for the measurement of small SSA samples by the BET method. The vapor pressure of krypton is much lower than that of methane at −195.8 °C. To the best of our knowledge, krypton has not been used for measuring the SSA of snow.

The BET method using methane and krypton requires liquid nitrogen for the adsorption process; however, it seems difficult to prepare liquid nitrogen in the field, and transportation of liquid nitrogen is also restricted. For example, it is impossible to transport liquid nitrogen by means such as airplane, helicopter, and ship. Hexane (normal alkane, n-C_6H_{14}) has a vapor pressure of the same order (around 1 kPa) at −21.3 °C, which is the eutectic point of a mixture of NaCl and H_2O. The preparation of “salt and snow” is easy. Therefore, hexane might be applicable for measuring the SSA of snow without liquid nitrogen.

We constructed a system for measuring the SSA of snow by a gas adsorption method according to Legagneux et al. (2002). In this study, we measured the SSA of synthetic ice particles and natural snow in Hokkaido, Japan and at-

Corresponding author address: Akihiro Hachikubo, Kitami Institute of Technology, 165 Koencho, Kitami 090-8507, Japan;
tel: +81-157-26-9522; fax: +81-157-26-9534;
email: hachi@mail.kitami-it.ac.jp

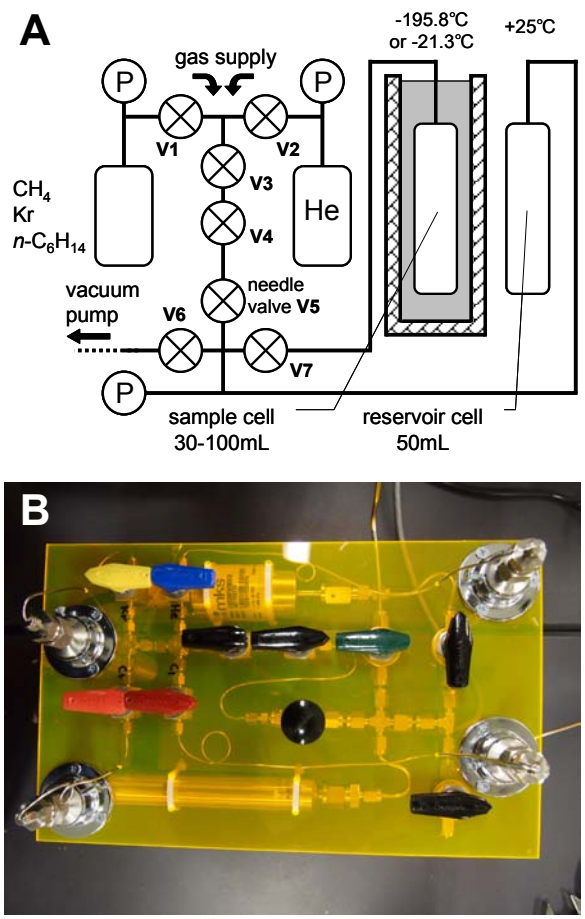


Figure 1. **A** Schematic view of the apparatus. **B** Photo of the main device. P: manometers.

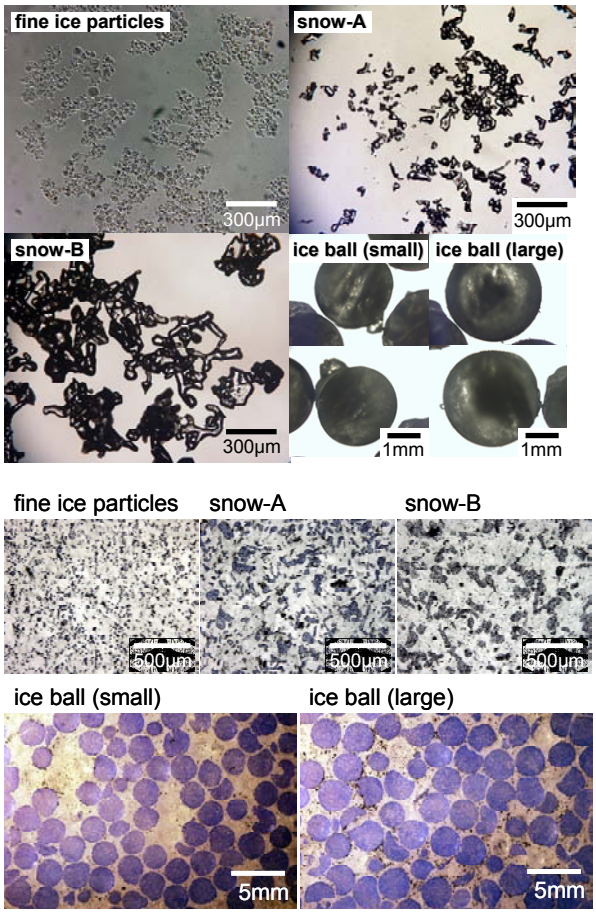


Figure 2. Photographs of ice and snow particles and their section planes.

tempted to use not only methane but also other adsorbents such as krypton and hexane.

2 METHODS AND MATERIALS

2.1 Apparatus

The method and principles have been described in detail by Legagneux et al. (2002). A schematic view of our device is shown in Figure 1. The main device is composed of pressure cells, tubes made of stainless steel, and greaseless valves. The basic performance of the device was reported by Hachikubo et al. (2012).

When using methane as an adsorbent, approximately 10 g of a snow sample was put into a sample cell (stainless steel; standard size 30-mL) and immersed in liquid nitrogen to maintain temperature at −195.8 °C. Methane introduced into the reservoir cell via the valves V1, V3, V4, and V5 was diffused into the sample cell through the valve V7 and partly adsorbed to the surface of snow particles. The adsorption amount can be calculated by comparing the result using helium because helium cannot be adsorbed. We obtained the dataset of the relation between the amount of methane adsorption and the pressure of methane. We applied the BET method to obtain the surface area of the sample and the heat of adsorption of methane on the ice surface. We adopted 0.1918 nm^2 as the molecular cross-sectional surface area of methane on ice (Chaix et al., 1996).

We also applied krypton and hexane as adsorbents. The vapor pressure of krypton at −195.8 °C is 331 Pa, which is lesser than that of methane (1294 Pa, Legagneux et al., 2002), indicating that krypton seems to be suitable for the relatively smaller SSA of snow. On the other hand, the vapor pressure of hexane is 1717 Pa at −21.3 °C, which corresponds to the eutectic point of a mixture of NaCl and H_2O. Therefore, simply salt and water are needed for a cryogen, without liquid nitrogen.

Legagneux et al. (2004) and Dominé et al. (2007) pointed out that the adsorption of methane on the inner wall of the sample cell was not negligible. Therefore, we measured the surface area of the sample cell and subtracted it from the measured data.

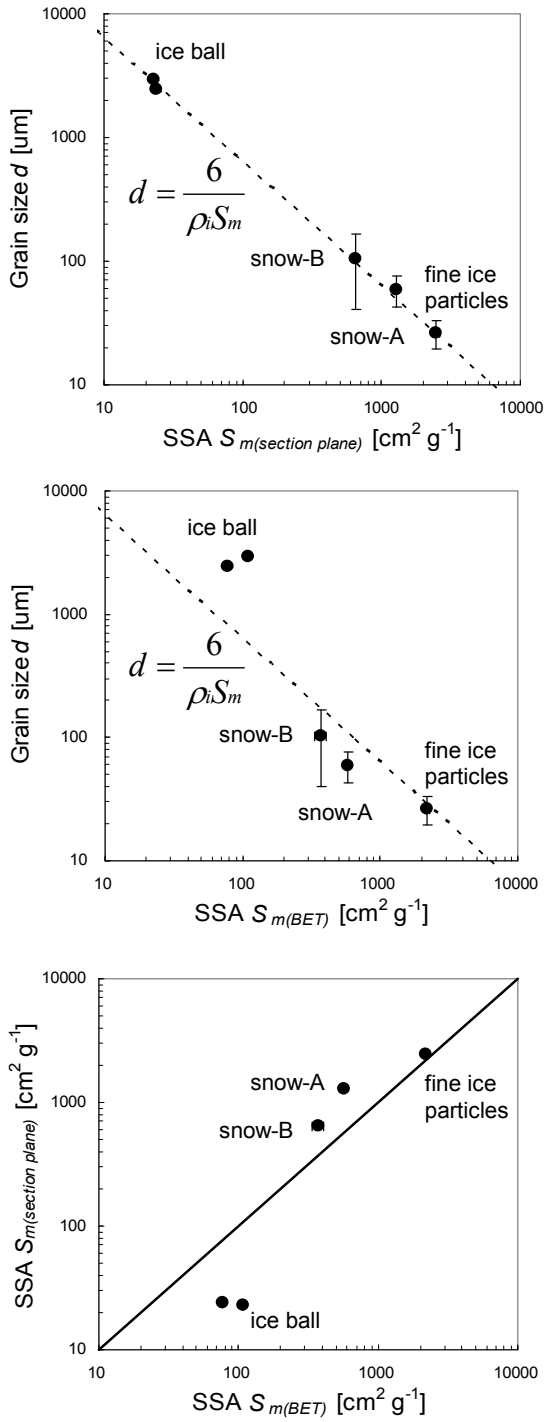


Figure 3. Relations between grain size and SSA by the BET and stereological methods, respectively. The dashed line corresponds to spherical particles based on the grain size; ρ_i is the density of ice.

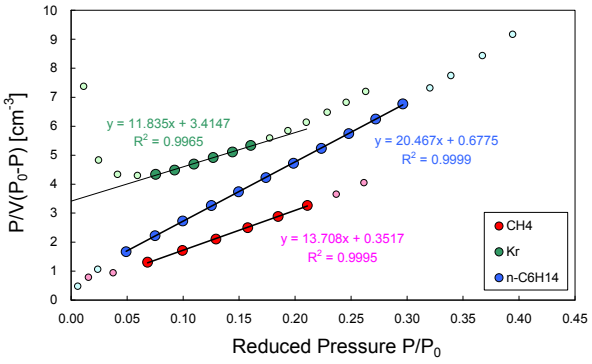


Figure 4. BET plots for different adsorbents. Snow samples were obtained in March 2012, stored at −50 °C, and measured in November 2012.

2.2 Samples

To check for a relation between SSA measurements obtained by the BET and stereological methods (e.g., Narita, 1969; 1971; Arakawa et al., 2009), we prepared fine ice particles (mean diameter 26 μm), large and small ice balls (3.0 mm and 2.4 mm, respectively), and two kinds of natural snow (partly decomposed precipitation particles, snow-A and -B). Photographs and section planes of these samples are shown in Figure 2. The fine ice particles were made from mist generated using an ultrasonic humidifier and trapped in liquid nitrogen and the ice balls were made from droplets of distilled water trapped in liquid nitrogen.

Section planes of these samples were prepared to measure the SSA by the stereological method. Snow samples were immersed in dodecane ($C_{12}H_{26}$) and were frozen in a cold room (−20 °C). The ice surface of the section planes of the samples were dyed with water blue (aniline blue, $C_{32}H_{25}N_3O_9S_3Na_2$), which is a water-soluble stain (Narita, 1969; Hachikubo et al., 2000). Grain-size analysis for these particles was also executed.

In the winter seasons of 2011–2012 and 2012–2013, we measured the SSA of the same natural snow samples obtained from the same layer for comparison between different adsorbents.

3 RESULTS AND DISCUSSION

Legagneux et al. (2002) showed that the repeatability of a measurement was less than 2% (standard deviation). We measured the SSA of the same snow sample more than five times and found that the standard deviation of the SSA using methane was approximately 3%, indicating that the performance of our device was generally equivalent to that of the previous study.

3.1 Comparison between grain size and the SSA

We checked for a relation between grain size and SSA by the stereological method (Figure 3a). The dashed line shows the SSA esti-

Table 1. SSA values and heats of adsorption calculated from the data of Figure 4.

adsorbent	SSA [$cm^2\ g^{-1}$]	heat of adsorption [$J\ mol^{-1}$]
CH_4	326 ± 3	2455 ± 21
Kr	337 ± 7	984 ± 69
n-C_6H_{14}	744 ± 25	2199 ± 60

mated from the grain size, supposing that the snow particles were spherical. The data were fairly plotted on the relation of spherical particles, although snow-B had a wide distribution in grain size. On the contrary, the SSA data by the BET method deviated from the line of spherical particles (Figure 3b). The SSA by the BET method was underestimated compared to that by the stereological method in the case of natural snow (snow-A and -B) and overestimated for the ice balls (Figure 3c). Because the effect of the inner wall of the sample cell was already accounted for, it is possible that the surface of the ice balls was microscopically rough.

3.2 New adsorbents: krypton and hexane

The SSA of the same snow sample stored in the cold room was measured using different adsorbents, and reasonable BET plots were obtained (Figure 4). The SSA and heat of adsorption data are summarized in Table 1. The snow sample was composed of decomposing and fragmented precipitation particles that were stored for approximately 9 months at −50 °C. SSA measurements using methane and krypton were comparable, although the measurement obtained using hexane seemed to be twice as large. The heat of adsorption was 2455±21 J mol^{-1} for methane, which agrees well with the 2540±200 J mol^{-1} recommended by Dominé et al. (2007). Although krypton is applicable for measuring the SSA of snow, we found that it took a considerable time to reach a steady state for adsorption. The heat of adsorption of krypton was smaller than that of methane.

Figure 5 shows a relation between the SSA data using hexane and methane. We obtained the dataset from fine precipitation particles to coarse melt forms and found that the data by hexane is always larger than that by methane. We need significantly more data to obtain a conversion equation between the data obtained using the two adsorbents. We also must check the exact molecular cross-sectional surface area of hexane on ice.

Methane and krypton require liquid nitrogen as a cryogen for the snow samples, which makes it difficult to apply the gas adsorption method in fieldwork. Therefore, the method using hexane is attractive and interesting because

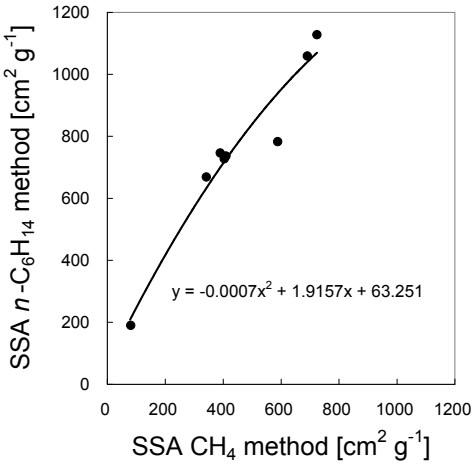


Figure 5. Relation between SSA by hexane and methane.

it only requires preparing salt: we can mix salt with snow to make a sufficient cryogen. However, we need to consider the effect of water-vapor pressure, which is approximately 92 Pa at −21.3 °C. In the calculation of the SSA, we subtracted the contribution of water vapor from the pressure data, supposing that the adsorption process of hexane was independent from the sublimation process of water. It is still unknown how the equilibrium process between an adsorptive medium and its vapor affects the adsorption process. Besides, hexane has the potential to erode the ice surface (Mae, personal communication). We also aim to find other adsorbents suitable for measuring the SSA of snow.

4 CONCLUDING REMARKS

We made a device for measuring the SSA of snow by the BET method using methane adsorbent and attempted to use krypton and hexane as new adsorbents. Although methane is currently the best adsorbent for the SSA of snow, the process requires liquid nitrogen. The ability to use a mixture of salt and ice (snow) as the cryogen is highly advantageous for fieldwork. The ideal adsorbent has a vapor pressure of approximately 1 kPa at −21.3 °C. Although some halomethanes (e.g., carbon tetrachloride, dichloromethane, and chloroform) fit this condition, they are often toxic and cause environmental damage.

On the other hand, vapor shippers (dryshippers) can be sent to a mountainous area so as to cool and store the snow samples with a pressure cell. A vapor shipper can maintain the temperature of liquid nitrogen and be sent by airplane. We can obtain snow samples in the field, store them at liquid nitrogen temperature, and return them to the laboratory. This is another possible approach for applying the BET method in the field.

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